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Infrared Spectra and Molecular Constants of Isotopic Nitrous Oxides

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The high resolution infrared spectrum of ordinary nitrous oxide, $^{14}N_2{}^{16}O$, has recently been the subject of extensive investigations, in particular at the National Bureau of Standards (1) and at the Pennsylvania State University (2,3). The vibrational and rotational constants of the $^{14}N_2{}^{16}O$ molecule are fairly well known from the former investigation (1), although some of the accurately measured higher levels (2) are not in very good agreement with values calculated from these molecular constants.

In order to establish the potential function and the structure of the nitrous oxide molecule, accurate vibrational and rotational constants of isotopically substituted nitrous oxides are required. However, the rotation-vibration spectra of the isotopic molecules have been studied much less extensively. The fundamentals and some overtones of $^{15}N^{14}N^{16}O$, $^{15}N_2{}^{16}O$, and $^{14}N^{15}N^{16}O$ have recently been measured under low resolution by Begun and Fletcher (4); these authors estimated the anharmonic constants of these molecules from the $^{14}N_2{}^{16}O$ vibrational constants (in which Fermi resonance had been neglected) using approximate isotopic relations and obtained an approximate potential (quadratic) for nitrous oxide. A high resolution study of some overtone bands of $^{15}N^{14}N^{16}O$ was made by Douglas and Møller (5) who were able to obtain equilibrium moments of inertia for this species and for the ordinary molecule and calculated the internuclear distances.

The present study was undertaken in the hope of locating some of the vibration-rotation levels of two isotopic nitrous oxides, $^{15}N^{14}N^{16}O$ and $^{15}N_2{}^{16}O$, with high precision, which, together with known vibrational and rotational constants of the ordinary molecule, would make possible a complete determination of the potential function involving the quadratic, cubic, and quartic terms. This was of particular interest in connection with our previous studies of the anharmonic terms of potential functions (6).

Experimental

The $^{15}N^{14}N^{16}O$ and $^{15}N_2{}^{16}O$ gases used in this work were stated to be of 97% and 99% isotopic purity respectively.

The spectra were recorded with a grating infrared Spectrometer at the Division of Pure Physics, National Research Council, Ottawa, Canada,

which has been described by Douglas and Sharma (7). Great care was given to the wavenumber measurement: with the present instrument, the most reliable procedure was found in the use of accurately known CO, HCN, and HCl lines (2,8) as standards with which one can calibrate the absolute scale of the Fabry-Perot fringe system (7) used for interpolation between standard lines. It is believed that the absolute positions of unblended lines measured in this way can be determined to within 0.02 cm^{-1}.

Results and Discussion.

Eleven bands of each isotopic molecule were measured in the region 2100-4450 cm^{-1} together with the corresponding $^{14}N_2{}^{16}O$ bands remeasured for comparison. Such a comparison was thought necessary in order to secure the same absolute scale for all species; this is important since the isotopic shifts rather than the absolute values are most critical in potential constant and structure calculations. The band centres, rotational constants, and centrifugal distortion constants obtained from an analysis of these bands are listed in Table I. The analysis was carried out using the microwave ground state rotational constants (9,10): for $^{14}N_2{}^{16}O$, B_o 0.419011, D_o 179×10^{-9} cm^{-1}; for $^{15}N^{14}N^{16}O$, B_o 0.404856, D_o 165×10^{-9} cm^{-1}; for $^{15}N_2{}^{16}O$, B_o 0.404859, D_o 166×10^{-9} cm^{-1} (the distortion constants for the isotopic molecules were estimated from isotopic relations).

For two of the hot bands the upper levels were also observed in ground state bands (cf.Table I); with the aid of the Ritz combination principle constants of the bending fundamental, ν_2^1 , were calculated.

From the rotational constants given here improved values of the equilibrium internuclear distances were obtained. Using the constants of the 001 level and of the sum of the Fermi resonance diad 101 and $02^0 1$ for obtaining the correction for rotation-vibration interaction, the equilibrium rotational constants, moments of inertia and internuclear distances given in Table II were calculated.

The number of vibrational levels measured in this investigation is not sufficient for a complete independent determination of all vibrational constants of the individual isotopic species. However, from the vibrational constants of $^{14}N_2{}^{16}O$ published recently by Tidwell, Plyler, and Benedict(1), it is possible to estimate the values of some of the missing constants with the aid of isotopic relations. A set of anharmonic constants and zero-order frequencies thus obtained is listed in Table III together with a set of quadratic potential constants obtained by a least squares procedure from

Table I

Observed N_2O Bands*

Band	$^{14}N_2{}^{16}O$			$^{15}N^{14}N^{16}O$			$^{15}N_2{}^{16}O$			
	ν_0	B'-B''	D'-D''	ν_0	B'-B''	D'-D''	ν_0	B'-B''	D'-D''	
ν_3	2223.754	-3447	0	2201.605	-3360	0	2154.731	-3245	0	
$\nu_2^1+\nu_3$	2798.288	-3237	0	2772.709	-3141	0	2713.144	-3066	0	
	Q	-2464	0	Q	-2417	0	Q	-2317	0	
$2\nu_2^0+\nu_3$	3363.978	-2478	+60	3333.731	-2437	+56	3264.702	-2289	+69	
$\nu_1+\nu_3$	3480.856	-5240	- 6	3443.659	-4980	- 5	3394.185	-4970	- 3	
$2\nu_3$	4417.383	-6926	0	4373.613	-6740	0	4281.343	-6505	0	
$\nu_2^1+\nu_3-\nu_2^1$	2209.521	-3412	0	2187.387	-3325	0	2141.255	-3213	0	
$2\nu_2^0+\nu_3-\nu_2^1$	2775.209	-2625	+60	2748.427	-2614	+56	2692.820	-2428	+69	
	Q	-3417	+60	Q	-3356	+56	Q	-3190	+69	
$2\nu_2^2+\nu_3-\nu_2^1$	2784.371	-2425	-54	2758.813	-2387	-51	2699.939	-2283	-66	(c-c)
		-3215	0		-3129	0		-3045	0	(d-d)
$3\nu_2^1+\nu_3-\nu_2^1$	3342.468	-2895	+30	3311.453	-2887	+30	3245.377	-2688	+30	(c-c)
		-2255	+33		-2284	+30		-2014	+33	(d-d)
$\nu_1+\nu_2^1+\nu_3-\nu_2^1$	3473.221	-5057	- 8	3436.970	-4818	- 7	3385.861	-4868	- 6	
$\nu_2^1+2\nu_3-\nu_2^1$	4388.910	-6838	0	4345.195	-6642	0	4254.396	-6425	0	
ν_2^1	588.767	+ 166	0	585.321	+ 174	0	571.887	+ 142	0	
	Q	+ 958	0	Q	+ 916	0	Q	+ 904	0	

*ν_0 cm^{-1}; B'-B''10^{-6} cm^{-1}; D'-D''10^{-9} cm^{-1}.

Table II

Structure Determination

Constant	$^{14}N_2{}^{16}O$	$^{15}N^{14}N^{16}O$	$^{15}N_2{}^{16}O$
B_o (cm^{-1})	0.419011	0.404856	0.404859
$\alpha_1+2\alpha_2+\alpha_3$ (cm^{-1})	0.004271	0.004057	0.004014
B_e (cm^{-1})	0.421146±.000015	0.406884±.000015	0.406866±.000015
I_e (10^{-40} gcm^{-2})	66.4482±.0020	68.7773±.0020	68.7804±.0020
r_{N-N} (Å)	1.1281±.0005		
r_{N-O} (Å)	1.1841±.0005		

these zero-order frequencies.

It was mentioned that the vibrational constants of $^{14}N_2{}^{16}O$ reported by Tidwell, Plyler, and Benedict (1) are not entirely satisfactory; it is therefore planned to reevaluate these constants using some more recent

Table III

Vibrational and Quadratic Potential Constants*

	$^{14}N_2{}^{16}O$	$^{15}N^{14}N^{16}O$	$^{15}N_2{}^{16}O$		$^{14}N_2{}^{16}O$	$^{15}N^{14}N^{16}O$	$^{15}N_2{}^{16}O$
ω_1^o	1280.83	1264.03	1262.68	x_{12}	-0.65	-0.64	-0.61
ω_2^o	588.59	585.16	571.75	x_{13}	-27.30	-26.68	-26.06
ω_3^o	2238.79	2216.40	2168.79	x_{23}	-14.20	-14.21	-13.48
ω_1	1299.29	1282.25	1280.55	x_{ll}	+0.73	+0.72	+0.69
ω_2	596.39	592.79	578.99	k_{122}	-44.69	-44.13	-43.08
ω_3	2281.41	2258.75	2209.35	W_o	-30.24	-29.87	-29.17
x_{11}	-4.36	-4.24	-4.23	λ_1	0.39	0.38	0.38
x_{22}	-0.10	-0.10	-0.09	λ_2	0.26	0.26	0.25
x_{33}	-15.03	-14.80	-14.06	λ_3	0.87	0.85	0.82
$K(q_{NN}^2)$	18.202	$K(q_{NO}^2)$	11.995	$K(q_{NN}q_{NO})$	+1.021	$K(\gamma_{NNO}^2)$	0.6653

*Vibrational constants in cm^{-1}, potential constants in 10^5 d/cm.

accurate data (2,3) together with some of the results of the present measurements. It is believed this will also yield more reliable constants for the isotopic derivatives; thus an accurate picture of the quadratic, cubic, and quartic part of the potential function of nitrous oxide should be achieved.

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On the Anomalous Splittings of the Multiplet States in Diatomic Molecules II

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It has been shown in two previous papers [1], [2] that the "anomalous multiplet splittings" of the $X^2\Sigma^+$ term of the AgH molecule, the $B^2\Sigma$ term of the YO molecule, the $A^3\Sigma_\mu^+$ and $B'^3\Sigma_\mu^-$ terms of the N_2 molecule, as well as the $^7\Sigma$ term of the MnH molecule can be excellently interpreted theoretically as the perturbations of not too far lying Π terms. The experimental examples mentioned above show that such anomalous splittings may occur quite often and upon their occurence the interpretation of the phenomenon was difficult, because theory was then lacking. Working on bases similar to the previous, the present paper aims at extending the theory to the anomalous splittings that may be expected in the case of the as yet missing Σ terms, namely $^4\Sigma$, $^5\Sigma$, $^6\Sigma$ terms; wishing thus to meet half-way, and render help to, the experimental research worker.

As is well known, for the dependence on the rotational quantum number of the components of multiplet Σ terms such relatively simple formulas are valid that can be arrived to after solving the separated wave equation and taking into account the mutual perturbations of the components belonging to Hund's case a), completed with the perturbation terms of the spin-spin interaction, as well as the interaction between rotation and spin [3]. Deviations from the formulas thus gained are called "anomalous splittings."

If, when using the terms neglected at the separation of the wave equation and those of the spin-orbit interaction, the perturbations of the Σ and Π states of the same and different multiplicity are taken into account, then, if the states mentioned are lying far enough, these perturbations will not change the structure of the Σ term formulas mentioned above, i.e. their dependence on the rotational quantum numbers, but, apart from a little constant displacement only the values of the constants in the original formulas will be modified [4], [2].

However, if the perturbing terms are lying nearer to the Σ terms at issue so that the changing of their distance with the rotational quantum number cannot be neglected, then, beside the changes in the value of the constants, such correctional terms will also occur as will bring about changes in the structure of the formulas; in other words, the dependence on the rotational quantum number of the original formulas will also change. These new additional terms will excellently describe the anomalous multiplet splittings in each of the cases observed so far.

A detailed course of the calculations can be found in earlier works [1], [2]; here only the final results are given for the missing cases, as well as a little more exact form of the earlier derivated formula for the case of the $^{?}\Sigma$ term.

Denote $\overline{F_i(N)}$ the terms observed as unperturbed for the experimental research worker / i.e. such terms where the values of the original constants have changed, but the structure of the formulas remained the same /; $F_i'(N)$ the actually ob-

served, that is perturbed, terms; then $\Delta F_i(N) = F_i'(N) - \overline{F_i(N)}$ means the deviations measured from the original formulas. For this we have the following:

In case of $^4\Sigma$ terms:

$$\begin{aligned}
\Delta F_1(N) &= -[3\sigma(N+1) - \tau]N^2 \\
\Delta F_2(N) &= -[\sigma(N-3)(N+1) + \tau(N+3)]N \\
\Delta F_3(N) &= +[\sigma N(N+4) - \tau(N-2)](N+1) \\
\Delta F_4(N) &= +[3\sigma N + \tau](N+1)^2
\end{aligned} \tag{1}$$

where

$$\sigma = 4\frac{\xi\eta(B_\pi - B_\Sigma)}{(h\omega)^2} \qquad \tau = \frac{\xi^2(B_\pi - B_\Sigma)}{(h\omega)^2} \tag{2}$$

and ξ is the constant occurring in the matrix elements of the spin-orbit interaction, η is that of the interaction coming from the terms neglected at the separation of the wave equation, B_Σ and B_π are the unperturbed values of the rotational constants of the perturbed and perturbing terms, occurring in the original multiplet formulas / that is, not those occurring in the $\overline{F_i(N)}$ / and finally $h\omega$ is the difference between the corresponding vibrational states of the perturbed and perturbing terms.

In case of $^5\Sigma$ terms:

$$\begin{aligned}
\Delta F_1(N) &= -[\sigma(2N+3)(N+1) - 2\tau(2N+1)]N \\
\Delta F_2(N) &= -[\sigma(N+1)^2 - \tau(N-4)]N \\
\Delta F_3(N) &= 0 \\
\Delta F_4(N) &= +[\sigma N^2 + \tau(N+5)](N+1) \\
\Delta F_5(N) &= +[\sigma(2N-1)N + 2\tau(2N+1)](N+1)
\end{aligned} \tag{3}$$

where

$$\sigma = \frac{8\xi\eta(B_\Pi - B_\Sigma)}{(hc)^2} \quad ; \quad \tau = \frac{\xi^2(B_\Pi - B_\Sigma)}{(hc)^2} \tag{4}$$

In case of $^6\Sigma$ terms:

$$\begin{aligned}
\Delta F_1(N) &= -5[\sigma(N+1) - \tau]N^2 \\
\Delta F_2(N) &= -[\sigma(3N-5)(N+1) + \tau(N+15)]N \\
\Delta F_3(N) &= -[\sigma N(N+1)(N-8) + 2\tau(2N-3)(N+4)] \\
\Delta F_4(N) &= +[\sigma N(N+1)(N+9) - 2\tau(2N+5)(N-3)] \\
\Delta F_5(N) &= +[\sigma(3N+8)N - \tau(N-14)](N+1) \\
\Delta F_6(N) &= +5[\sigma N + \tau](N+1)^2
\end{aligned} \tag{5}$$

where

$$\sigma = 4\,\frac{\xi\eta(B_\Pi - B_\Sigma)}{(hc)^2} \quad ; \quad \tau = \frac{2}{3}\,\frac{\xi^2(B_\Pi - B_\Sigma)}{(hc)^2} \tag{6}$$

In case of $^7\Sigma$ terms:

$$\begin{aligned}
\Delta F_1(N) &= -[36(N+1)(N+2) - \tau(9N+4)]N \\
\Delta F_2(N) &= -[6(N+1)(2N+3) - \tau(4N-11)]N \\
\Delta F_3(N) &= -[6N(N+1)^2 - \tfrac{1}{2}\tau(N-5)(2N-9)] \\
\Delta F_4(N) &= 0 \\
\Delta F_5(N) &= +[6N^2(N+1) + \tfrac{1}{2}\tau(N+6)(2N+11)] \\
\Delta F_6(N) &= +[6N(2N-1) + \tau(4N+15)](N+1) \\
\Delta F_7(N) &= +[36(N-1)N + \tau(9N+5)](N+1)
\end{aligned} \tag{7}$$

where the value of σ and τ is identical with (4) .

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The Molecular Complex of Diphenylketone with Iodine

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In the course of studying the interaction among the π-electrons in some derivatives of diphenylmethane, it seemed of interest to examine the "charge transfer" phenomenon between diphenylketone (benzophenone, B.P.) and iodine.[1,2] As we will show in the last part of this work, the possibility - from a molecular point of view - of the formation of a "charge-transfer" complex between B.P. and iodine, is evident. The present work contains the results of a spectrophotometric study of this complex in carbon tetrachloride.

Experimental

Resublimed iodine, B.P. (Veb. Laborchemie Apolda) and carbon tetrachloride (Veb. Feinchemie Eisenach) were used.

Sample preparations were made according to the usual recommendations [1,3] special attention being paid to the variation of concentration of the solutions with temperature.

A VSU-1 C. Zeiss-Jena spectrophotometer (with tested accuracy for wave-length and photometric-attachment scales), matched one centimeter stoppered quartz cells, and a thermostatic attachment for the cells connected to a Wöbser thermostat, were used.

The measurements were made in a concentration range of 0.1 to 0.8 mole liter^{-1} for B.P. and 0.0008 to 0.0022 mole. liter^{-1} for iodine.

Results

Although the solutions of B.P. plus iodine in carbon tetrachloride absorb strongly in nearly all visible and ultraviolet ranges, it was possible to detect a "blue shift" in the spectra of solutions in the region 4600 - 4800 Å (region of the "blue shift" absorption [4]). Only iodine absorbs in this region, in accordance with the Beer law [5]. Assuming a 1:1 complex formation and using the Rose-Drago [6] treatment of data for the system:

$$I_2 + \text{B.P.} \rightleftharpoons \text{Complex},$$

the reciprocal values of the equilibrium constant K at a given wave-length, were obtained from the equation:

$$K^{-1} = \frac{A - A^0}{\varepsilon_c - \varepsilon_i} - C_i - C_D + \frac{C_D C_i (\varepsilon_c - \varepsilon_i)}{A - A^0}$$

where $C_{D(i)}$ = initial B.P. (iodine) concentration, in mole liter^{-1}.

$\varepsilon_{C(i)}$ = complex (iodine) molar absorptivity.

A = solution absorbance per unit of optical path.

A^0 = $\varepsilon_i C_i$ (the absorbance of the initial concentration of iodine).

The following data were obtained at 23°C and λ = 4600 Å (ε_i = 233):

ε_c	$\frac{C_D C_i}{A - A^\circ}(\varepsilon_c - \varepsilon_i)$	K^{-1}
600	1.1955	0.9947
650	1.3225	1.1227
700	1.4515	1.2506
750	1.5795	1.3786
800	1.7075	1.5060

The values of K and ε_c were found graphically by plotting K^{-1} as a function of ε_c at various C_D values:

$K = 0.76 \pm 0.05$ liter mole^{-1}
$\varepsilon_c = 820 \pm 25$ liter mole^{-1} cm^{-1}

From the values of K at various temperatures, the heat of complex formation was obtained:

$\Delta H = 2.0 \pm 0.5$ kcal.mol.$^{-1}$

Using Ketelaar's method [7] at three wave-lengths, we obtained:

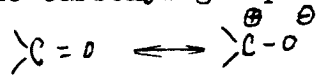
λ (Å)	$K(\varepsilon_c - \varepsilon_i)10^{-3}$	K
4.600	0.40	0.91
4.700	0.52	1.10
4.800	0.46	0.95

in satisfactory agreement with the former value.

Discussion

Assuming a planar configuration of B.P., the π-electrons

form a unified aromatic system, with a greater charge-density at the oxygen atom than at any of the carbon atoms. Now, according to a SCF-MO calculation [8], this charge-density is greater in B.P. than in other common aromatic ketones (benzaldehyde, fluorenone, benzyl, etc.). This ionic resonance of the carbonyl group:



is fairly well proved by the chemical properties of numerous compounds, and especially in the case of B.P. as an intermediate stage in the mechanism of polarographic reduction[9,10] as well as in the formation, for example, of metal-ketyls (B.P. is quoted as a typical example[11]).

It follows from the above considerations that the tendency of B.P. to form a charge-transfer complex is appreciable. It is probably that an oxygen lone pair of electrons is responsible for the bond formation. But when considering the factors contributing to the stability of the complex, in addition to charge-transfer delocalisation we shall take account of dispersion forces [12].

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ELECTRON AND VIBRATION SPECTRA OF INDANE HYDROCARBONS

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This paper gives the results of a study of the electron and vibration spectra of indane derivatives containing one, two and three alkane or cycloalkane substituents synthesised by E.S.Pokrovskaya and coworkers (I,6).The spectra of indane homologues with substituents in the naphtene ring are close and similar to those of indane.The electron spectra of indane derivatives with substituents in the benzene ring have identical intensity distributions in the absorption band but are displaced 5 to I5 Å.The absorption spectrum of ethylindane occupies the most longwave position compared to those of isopropyl- and 2-ethylhexylindane which possess hihgly branched substituents.A similar shift is observed in the spectra of certain isomeric butylbenzenes (2) and alkyl benzenes (3). The common absorption band shape of monosubstituted indanes and their common position on the wave-lengh scale with allowance for insignificant displacements due to the structure of their chains gives grounds to assume that the 5-substituted indane derivatives are of similar structure.Comparison of these spectra with the known spectra of methylindanes with methyl groups in the benzene ring suggests that the substituent groups in the indanes studied is in the β-position, as was assumed on the basis of the conditions of synthesis(I). The intensity and position of the absorption maxima in the spectra of diethyl-isopropyl- and diisobutylindanes are close

to each other, this being an indication that the hydrocarbons in question are of the same structure type; the 5,6- substitution type is the most probable.The five-membered ring in the indane molecule radically alters the nature of the electron absorption spectrum, increasing the absorption intensity by several times and strengthening the vibration structure. Possibly the introduction of several sufficiently heavy substituent groups into the benzene nucleus of indane will deform the molecule to some extent and the vibration of di- and trisubstituted indanes will become close in nature to those of the corresponding tetra- and pentasubstituted benzenes.The spectra of tri-isopropyl- and tricyclohexylindanes with substituents in the benzene ring are still more similar to the spectrum of penta-substituted benzenes.The position and shape of the absorption band of indane hydrocarbons depends mainly on the number of substituent groups and their positions in the molecule.

A study was also made of the infrared absorption spectra of a number of indane derivatives in the 5-I5 micron range. The indane spectrum, though quite similar to the spectra of ortho-substituted benzenes (intensive double band in the 730-750 cm^{-I} range belonging to the out-of-plane deformation vibrations of the =C-H bonds of the benzene ring and a number of other bands) has also a number of specific absorption ranges.The spectrum of I-isopropylindane also has an intensive band in the 700-750 cm^{-I}range, indicating that the substitution type of the benzene ring has undergone no change and the substituent is therefore in the 5-membered cycle.The spect-

rum of I-cyclopentylindane is also similar to the first two, but additional bands of the monosubstituted cyclopentane ring appear additionally at 890 cm^{-I}. Both spectra are in good agreement with the spectrum of I-methylindane (4). It is not impossible, however, that both I-alkylindanes contain an admixture of the isomer with the substituent in the 2-position, because the characteristic band for 2-methylindanes is the intensive one at 935 cm^{-I}, and it has a weak maximum in the frequency range below 700 cm^{-I}. 5-methylindane gives a number of bands in the range of out-of-plane deformation vibration of the =C-H bond, the most intensive of which are characteristic of I,2,4-substitution of the benzene ring. Comparison of the spectra of 5-substituted indanes with that of 5-methylindanes reveals that all indane derivatives contain substituents not only in the 5-position but in the 4-position as well, this following from the high intensity of the 700 and 710 cm^{-I} bands relative to the 810 and 870 cm^{-I} bands. The structure of the same hydrocarbons determined by their electron spectra corresponded to 5-substitutions (5), as the percentage of 4-substituted hydrocarbons is relatively small, and their absorption in the ultraviolet is less intensive than that of the 5-substituted hydrocarbons. The absorption spectrum of I-isopropyl, 5-tertiarybenzylindane contains, apart from the bands belonging to the substituents, the characteristic bands of I,2,4-trisubstituted benzenes, and is similar in the 700-900 cm^{-I} range to the spectrum of I,6-dimethylindane which also possesses I,2,4-substitution in the benzene nucleus. From the conditions of synthesis (6) of dicyclopentylindane it is known

that both five-membered rings are substituents in the benzene ring. The only spectrum known in the literature is that of 4,7-dimethylindane, which has two bands in common with that of dimethyl dicyclopentylindane (810 and 720 cm^{-1}). But the most intensive band at 858 cm^{-1}, as well as the 1007 and 1028 cm^{-1} bands, are characteristic of I,2,4,5- and I,2,3,5-tetrasubstituted benzenes. Therefore, the dicyclopentylindane studied contained the 4,7- and 5,6- as well as the 5,7- isomers corresponding to I,2,3,5-substitution of the benzene ring. Thus, in the infrared absorption spectra of indane derivatives with one, two and three saturated C_I-C_{IO} substituents characteristic bands of various types of substituted benzenes are observed in the region of out-of-plane vibration of the =C-H bond. Taking advantage of the above indicated characteristic signs in the 5-15 micron range, as well as of the spectra of methylated indanes of known structure, the position of the substituents in various indane derivatives can be determined.

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ON THE CLASSIFICATION OF POINT GROUPS FOR MOLECULES

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As is well known, the classification of molecular energy states according to symmetry depends on the belonging of equilibrium configurations of molecules to definite point groups. The equilibrium configurations of molecules may in principle belong to every point group of finite order, and in the special case of linear molecules belong to point groups of infinite order $C_{\infty h}$ and $D_{\infty h}$/1/. A general classification of molecules with respect to the symmetry of their equilibrium configurations and the corresponding classification of point groups may be of interest. In the present communication such a classification is proposed in analogy to the classification of point groups for crystals /2/.

According to lattice symmetry crystals may belong to one of the 32 finite point groups for which the translational symmetry of the lattice is possible /3/. For crystals a more general classification into seven syngonies of three types is widely used: three lowest syngonies (triclinic, monoclinic, and rhombic), three middle syngonies (trigonal, tetragonal and hexagonal), and one highest syngony (cubic) /4/. In the case of the lowest syngonies no more-than-twofold axes of symmetry are present, for middle syngonies there is one more-than-twofold axis of symmetry (a distinguished axis), and for the highest syngony there are several more-than-twofold axes. The classification of crystals into these three types is the same as their classification with respect to optical properties: the crystals of lowest symmetry are biaxial, those of middle symmetry are monoaxial, and those of highest symmetry are optically isotropic /5,6/. A similar classification of molecules as molecules of lowest, middle and highest symmetry seems to be very useful.

For molecules of <u>lowest</u> symmetry with no axes of symmetry more-than-twofold, only nondegenerate vibrational and electronic states are possible. The physical properties differ in the directions of the three ortogonal axes; these molecules are

asymmetric tops (all three moments of inertia are different, $I_x \neq I_y \neq I_z$) and their polarization tensor is represented by an ellipsoid with three different semiaxes (all the principal polarizabilities are different, $\alpha_x \neq \alpha_y \neq \alpha_z$).

For molecules of middle symmetry with one distinguished more-than-twofold axis of symmetry (including the linear molecules with an infinityfold axis of symmetry C_∞) double degenerate vibrational and electronic states are possible*. Physical properties are different along the distinguished axis and along perpendicular directions; these molecules are symmetric tops ($I_x = I_y \neq I_z$, where z is the direction of the distinguished axis) and their polarizability tensor is represented by a rotation ellipsoid ($\alpha_x = \alpha_y \neq \alpha_z$).

For molecules of highest symmetry with several more-than-twofold axes, vibrational and electronic states are possible with a degree of degeneracy $r \geqslant 3$**. In the case of cubic symmetry triply degenerate states are possible. Physical properties along the ortogonal axes (for cubic symmetry along three fourfold axes) are identical; these molecules are spherical tops ($I_x = I_y = I_z$) and the polarizability tensor is represented by a sphere ($\alpha_x = \alpha_y = \alpha_z$).

According to the general classification of molecules and crystals with respect to their symmetry properties just described it is natural when applying the group theory to molecules and crystals to classify the point groups as groups of lowest, middle and highest symmetry.

Thus we have:

1. In the case of the absence of more-than-threefold axes of

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* Stable double degenerate electronic states for non-linear molecules are possible only if the Jahn-Teller theorem /7/ is not taken into account.

** Stable degenerate electronic states are again possible only if the Jahn-Teller theorem is not taken into account.

symmetry - groups of lowest symmetry C_1, C_{1v}, C_2, C_i, C_{2v}, D_2, C_{2h}, D_{2h};

2. In the case of one distinguished more-than-twofold axis of symmetry - groups of middle symmetry C_n, C_{nv}, D_n, C_{nh}, D_{nh} (integral $n \geq 3$) and S_n, S_{nv} (even $n \geq 4$).

3. In the case of several more-than-twofold axes of symmetry or of an infinite number of n-fold axes of symmetry (n arbitrary) - groups of highest symmetry T, T_h, T_d (tetrahedral groups), O, O_h (octahedral groups), I, I_h (icosahedral groups), R_{∞}, $R_{\infty h}$ (the infinite group of three-dimensional rotations not including and including inversion).

The classification of point groups is given in a table /8/. For finite groups their order is given in parenthesis The groups are arranged in the table according to the value of n for axes of symmetry (different lines correspond to different n) and the complication of the group by the addition of different symmetry elements to axes of symmetry. In the table are shown the most important properties of molecules depending on the different types of point groups to which the equilibrium configurations belong: the degree of degeneracy of vibrational and electronic states, the properties of the tensor of inertia and of the polarizability tensor, the non-zero values of the dipole moment.

The degree of degeneracy of vibrational and electronic states depends on the dimension of irreducible representations.

For groups of lowest symmetry all irreducible representations are one-dimensional as these groups are Abelian. Hence only non-degenerate vibrational and electronic states may occur for molecules of lower symmetry.

For groups of middle symmetry irreducible two-dimensional representations (for non-Abelian groups C_{nv}, D_n, S_{nv}, D_{nh}, $n > 3$) and pairs of complex conjugated one-dimensional representations (for Abelian groups C_n, S_n, C_{nh}, $n \geq 3$) are possible. Hence doubly degenerate (jointly or separably) vibrational and electronic states may occur for molecules of middle symmetry.

For groups of highest symmetry irreducible representations of dimension $r \geqslant 3$ are possible: three-dimensional for tetrahedral and octahedral groups, three-, four- and five-dimensional for icosahedral groups and of all dimensions for the infinite group of three-dimensional rotations. In the latter case well-known irreducible representations D_J of the dimension $2J + 1$ ($J = 0, 1, 2, \ldots$) are obtained /9/. For the most important case of molecules having cubic symmetry, i.e., for molecules belonging to tetrahedral and octahedral groups, triply degenerate vibrational and electronic states occur.

The properties of the tensor of inertia and of the polarizability tensor of a molecule that depend on its symmetry are special cases of the general properties of a molecule or of a crystal described by a symmetrical tensor of the second order /10/: for groups of lowest symmetry three different principal values are obtained ($T_x \neq T_y \neq T_z$), for groups of middle symmetry two different principal values are obtained ($T_x = T_y \neq T_z$), for groups of highest symmetry three identical principal values are obtained ($T_x = T_y = T_z$).

A non-zero value of the dipole moment is connected with the absence in the groups considered of symmetry operations that change the direction of the dipole moment. It is possible only for groups C_n and C_{nv} ($n = 1, 2, 3 \ldots \infty$) for a dipole moment along the distinguished axis of symmetry.

CLASSIFICATION OF POINT GROUPS

Type of Groups	Axes of Symmetry		Point Groups								Tensor Properties		
											Symmetrical Tensors of the Second Order	Tensor of Inertia	Polarisability Tensor
Groups of Lowest Symmetry	No more-than-two-fold axes, $n \leq 2$, $r = 1$	$n = 1$	$C_1(1)$		$C_{1v}=C_s(2)$					Crystal Groups	$T_x \neq T_y \neq T_z$	$I_x \neq I_y \neq I_z$ Asymmetrical top	$\alpha_x \neq \alpha_y \neq \alpha_z$
		$n = 2$	$C_2(2)$	$S_2=C_i(2)$	$C_{2v}(4)$	$D_2(4)$		$C_{2h}(4)$	$D_{2h}(8)$	Crystal Groups			
Groups of Middle Symmetry	One n-fold axis, $n \geqslant 3$, $r \leqslant 2$	$n = 3$	$C_3(3)$		$C_{3v}(6)$	$D_3(6)$		$C_{3h}(6)$	$D_{3h}(12)$	Crystal Groups	$T_x = T_y \neq T_z$	$I_x = I_y \neq I_z$ Symmetrical Top	$\alpha_x = \alpha_y \neq \alpha_z$
		$n = 4$	$C_4(4)$	$S_4(4)$	$C_{4v}(8)$	$D_4(8)$	$S_{4v}=D_{2d}(8)$	$C_{4h}(8)$	$D_{4h}(16)$	Crystal Groups			
		$n = 5$	$C_5(5)$		$C_{5v}(10)$	$D_5(10)$		$C_{5h}(10)$	$D_{5h}(20)$				
		$n = 6$	$C_6(6)$	$S_6(6)$	$C_{6v}(12)$	$D_6(12)$	$S_{6v}=D_{3d}(12)$	$C_{6h}(12)$	$D_{6h}(24)$	Crystal Groups			
			.....	.....	.....	.....	.....	.....	.....				
		$n = \infty$	$[C_{\infty}]$		C_{∞}	$[D_{\infty}]$		$[C_{\infty h}]$	$D_{\infty h}$				
Groups of Highest Symmetry	Several n-fold axes, $n \geqslant 3$	$r \leqslant 3$				$T(12)$			$T_h(24)$	Crystal Groups	$T_x = T_y = T_z$	$I_x = I_y = I_z$ Spherical Top	$\alpha_x = \alpha_y = \alpha_z$
		$r \leqslant 3$				$O(24)$	$T_d(24)$		$O_h(48)$	Crystal Groups			
		$r \leqslant 5$				$I(60)$			$I_h(120)$				
	Infinite number of infinity-fold axes	$\tau = 2j+1$				$[R_{\infty}]$			$[R_{\infty h}]$				
Dipole Moment P			$P \neq 0$	$P = 0$	$P \neq 0$	$P = 0$	$P = 0$	$P = 0$	$P = 0$				

Groups in square brackets cannot be realized for molecules (symmetry $R_{\infty h}$ is the symmetry of atoms).

Groups including the inversion are underlined.

r - degree of degeneration of vibrational and electronic states; J = 0, 1, 2, ...

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Spectral Investigation of Molecular Ion Formation on the Surface of Solids

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The spectra of aromatic amines, brought from the gas phase in vacuo in contact with disperse oxides (Al_2O_3, MgO) and gels (Al_2O_3, SiO_2, Al_2O_3-SiO_2, $Ca_3(PO_4)_2$) reveal two types of interaction with the surface: 1., a proton addition from acidic sites, 2., an electron donation to specific acceptor sites (1,2).

The protonic sites produce the known "blue" shift of the absorption spectrum of the basic molecule (aniline, β-naphthylamine) which disappears on exchange of the protons for Li^+, or Na^+ cations. The electron acceptor sites (presumably partially unscreened Al, Mg, Ca ions) are revealed by the appearance in the visible of the spectra of the positive molecular ion-radicals (diphenylamine, dimethyl paraphenylene diamine, benzidin) (2). Both types of sites are found on the mixed Al_2O_3-SiO_2 gel (cracking catalyst), whereas the interaction of the same compounds with the SiO_2 gel, or the pure Al_2O_3 gel does not produce any such spectral effects. The characteristic double band 520, 560 mμ of the positive ion-radical of dimethyl paraphenylene diamine is clearly exhibited on natural and synthetic Al_2O_3-SiO_2 gels. After the ionic exchange of the protons in these for Li^+ cations this double band still remains.

The visible absorption bands which appear on Al-Si gels upon adsorption of the aromatic amines mentioned, are accompanied by a strong ESR signal (10^{15} spins/cm^3, g= 2.004), confirming the presence of univalent molecular ions. No signal

is observed upon adsorption on the SiO_2 gel.

Electron acceptor sites have also been spectroscopically observed by Okuda and Tachibana for paraphenylenediamine adsorbed from a cyclohexane solution on a Al_2O_3-SiO_2 gel(3).

We have found that upon contact of the polyacene vapors (anthracene, tetracene, perylene) in vacuo with the Al_2O_3-SiO_2 gel surface there appear visible absorption bands shown in the Figs. 1, 2 and 3.

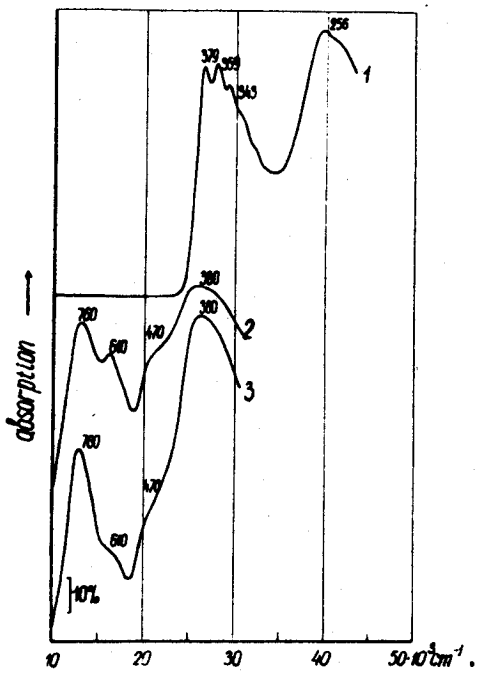

Fig.1 - Absorption spectra (diffuse reflexion) of anthracene, adsorbed on: 1- SiO_2gel; 2- Al_2O_3-SiO_2(30:70)gel; 3-the same after an H^+ exchange for Na^+.

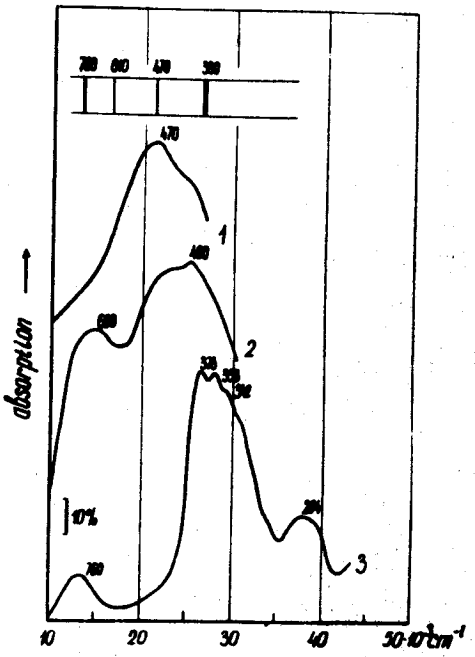

Fig.2 - Top: absorption maxima from spectrum 2 in Fig.1. Anthracene, adsorbed on: 1- strongly acidic ($-SO_3H$) cationite ; 2- $AlCl_3$; 3- $Ca_3(PO_4)_2$.

The structured band at 380 mμ ($26.3 \cdot 10^3 cm^{-1}$) belongs to anthracene molecules feebly interacting with the surface. The visible bands below $25 \cdot 10^3 cm^{-1}$, which appear only on Al_2O_3-SiO_2, but not on the SiO_2 gel (Fig. 1) belong to molecular species, formed as a result of a more deep interaction. In fact, the 470 mμ ($21.2 \cdot 10^3 cm^{-1}$) band is in the same range as that at 420-440 mμ, known for the carbonium AH^+ ion of anthracene (A), and observed in strong acids (4). In accordance with this interpretation it disappears, when the surface protons are replaced by Na^+ cations (Fig. 1, curve 3).

The 760 mμ ($13.2 \cdot 10^3 cm^{-1}$) band has about the same position as that of the A^+ ion (5) and evidently belongs to anthracene molecules, ionized by the strong electron acceptor sites existing on the Al_2O_3-SiO_2 gel surface. This band is accompanied by a strong ESR signal (10^{14} spins/cm^3, g=2.004), which does not disappear, but decreases to one third when the protons are exchanged for Na^+ cations.

The assignment of the 470 and 760 mμ absorption maxima is corroborated by the observation of the first when anthracene is adsorbed on a purely protonic organic adsorbent (Fig. 2, curve 1), and of the second one upon contact of anthracene vapor with solid $AlCl_3$ in vacuo (Fig. 2, curve 2).

Judging from the observation of the 760 mμ band and of of a ESR signal, the $Ca_3(PO_4)_2$ catalyst does also possess electron acceptor centers (Fig. 2, curve 3).

The origin of the 610 mμ ($16.4 \cdot 10^3 cm^{-1}$) absorption maximum (Figs. 1 and 2) is uncertain. We ascribe it to a π-coordinative bond of anthracene with Al atoms of the surface. This band is the only one appearing when anthracene vapor is adsorbed γ-Al_2O_3 disperse powder, without any ESR signal. After the Na^+ exchange in Al_2O_3-SiO_2 this band remains (Fig. 1, curve 3). Such coordination active sites are also revealed by the frequency increase of the C=N vibration

in CH_3CN (6), when adsorbed on the Al_2O_3-SiO_2 gel, comparable in magnitude to that observed under the action of electrophyllic agents, like $SnCl_4$, $AlCl_3$ (7).

The existence of electron acceptor sites on the Al_2O_3-SiO_2 is strikingly confirmed by the spectrum of perylene, adsorbed from the vapor in vacuo on it (Fig.3). The sharp absorption maximum at 534 mμ ($18.7 \cdot 10^3 cm^{-1}$) is the same that has been observed for perylene in concentrared H_2SO_4 at 530 mμ, and identified as belonging to its positive radical ion (8).

In accordance with this assignment a strong ESR signal with a hyperfine structure has been observed by us for perylene on Al_2O_3-SiO_2 (Fig.4). The maxima in the absorption spectrum

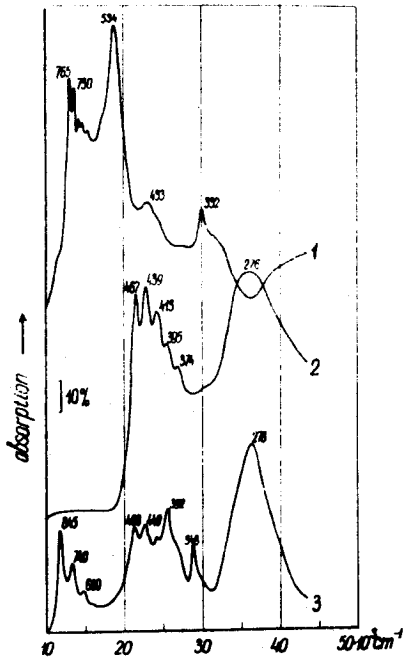

Fig.3 - Absorption spectra of: 1- perylene on Al_2O_3-SiO_2 (25:75) gel; 2- tetracene on SiO_2 gel; 3- tetracene on Al_2O_3-SiO_2(80:20)

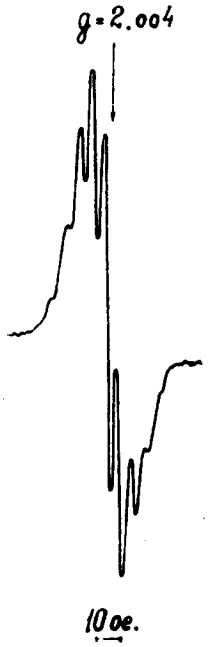

Fig.4 - ESR signal for perylene, adsorbed on Al_2O_3-SiO_2 (25:75) gel.

at 650,685,705,730,765,850 mμ are also seen in the spectrum of the perylene ion in H_2SO_4 (8).

The absorption maxima at 680,740,845 mμ (Fig.3,curve3) which appear when tetracene vapor is adsorbed on Al_2O_3-SiO_2, but not on SiO_2 (Fig.3,curve 2) can also be assigned to the corresponding molecular ion.

The specific dependence on the nature of the solid and on its thermal treatment under high vacuum conditions,without any contamination by a solvent,disproves the participation of oxygen traces in this phenomenon. This doubt has been expressed recently by Fogo,who observed a coloration and ESR signals for perylene and anthracene,adsorbed from evacuated benzene solutions on Al_2O_3-SiO_2 (9).

It has been reported by Roberts,Barter and Stone (10) that anthracene,adsorbed from decahydronaphtalene on Al_2O_3-SiO_2,gives rise to intense visible bands at 420 and 750 mμ, similar to those observed by us. Besides, they observed also feeble bands at 585 and 640 mμ,instead of the single one at 610 mμ in our case.All these maxima have been ascribed by the authors to the carbonium ion AH^+. According to our results this assignment is valid for the 420 mμ band only.

Instead of positive molecular ions,V.Lodin in our laboratory observed negative ion radicals when quinones were adsorbed from the vapor phase in vacuo on ZnO and other metal oxides.

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